

## Proton induced X-ray emission studies on Indian copper coins

V Vijayan\*, Pranaba K Nayak<sup>1</sup> and V Chakravortty<sup>1</sup>

Institute of Physics, Sachivalaya Marg, Bhubaneswar-751 005, Orissa

<sup>1</sup>Department of Chemistry, Utkal University, Vani Vihar, Bhubaneswar 751 004, Orissa

E-mail : vijayan@iopb.res.in

Received 6 May 2002, accepted 5 June 2002

**Abstract** Preliminary investigations on selected number of Indian copper coins were carried out using non-destructive PIXE technique. 3 MeV proton beam from a pelletron accelerator was used for irradiation of these samples. The computer code GUPIX was employed to get the elemental concentrations, and the obtained results are provided as well as discussed.

**Keywords** Non-destructive analysis, proton induced X ray emission (PIXE), analytical & quantitative method

**PACS Nos.** 82.50.Kx, 82.80.Ej

Coins are archaeological materials, and their analysis throws light on the economy and metallurgy of the minting time. These are valuable testimonials and provide accurate information on chronology. The evolution of coins, their changing design, shapes and markings, patterns and epigraphs conjure up before us a visual and factual picture of the contemporary culture. Also these are important in order to provide information regarding preparation methodology, provenance, and their classification plays a fundamental role in dating historical events, in constructing trade routes, in establishing the welfare of the nation [1]. Several nuclear techniques have been used for characterising various complex matrix systems [1-6]. Of these, nuclear analytical techniques like PIXE and EDXRF are especially suitable for analysis of archaeological samples as they are multielemental, simultaneous quantitative and non-destructive in nature. Proton induced X-ray emission (PIXE) technique is established as non-destructive, simultaneous multielemental, and was used previously for various arts and archaeological [3, 8, 10] studies. Compared to X-rays, protons other heavy charged particles have the advantage that electrostatic or electromagnetic lenses can focus them and they may be transported over large distances without loss of beam intensity. Hence compared to EDXRF, PIXE offers detection limits which are often one order of magnitude better [6, 7]. In

the present investigation, a preliminary attempt has been made to characterize Indian copper coins using PIXE technique.

A total of six coins were selected for the present study. Out of these samples, EIC-1 and EIC-2 are of East India Company (EIC) rule; BR-1 and BR-2 are of British rule, whereas H-1 and G-1 are of Holkar and Gwalior dynasty respectively.

The 3 MeV collimated proton beam, obtained from the 3MV Tandem pelletron accelerator at the Institute of Physics, Bhubaneswar, India, was used to irradiate the coins in vacuum ( $10^{-6}$  Torr) inside a PIXE chamber [5]. The targets were held at  $45^\circ$  to the beam direction. Measurements were carried out with low beam current (within 2-3 nA) in order to keep the count rate below 1000 cps. The Si(Li) detector (active area 30 mm<sup>2</sup>) of Canberra make with a resolution of 170 eV at 5.9 keV beryllium (8  $\mu$ m) window placed at  $90^\circ$  to the beam direction was used to detect characteristic X-rays emitted from the targets. X-rays exit the scattering chamber through a 95- $\mu$ m mylar window before entering the detector. The PIXE analysis was performed using GUPIX-2000 [9] software, which provides non-linear least squares fitting of the spectrum together with subsequent conversion of the X-ray peak intensities to elemental concentrations via a user-defined instrument constant, relative charge and X-ray dependent H value.

The elemental compositions of coins provided in the Table 1 representing the analysed PIXE data indicate that these coins

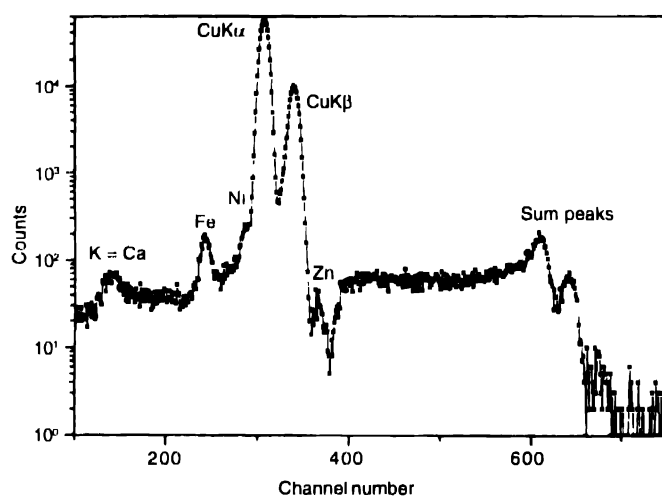
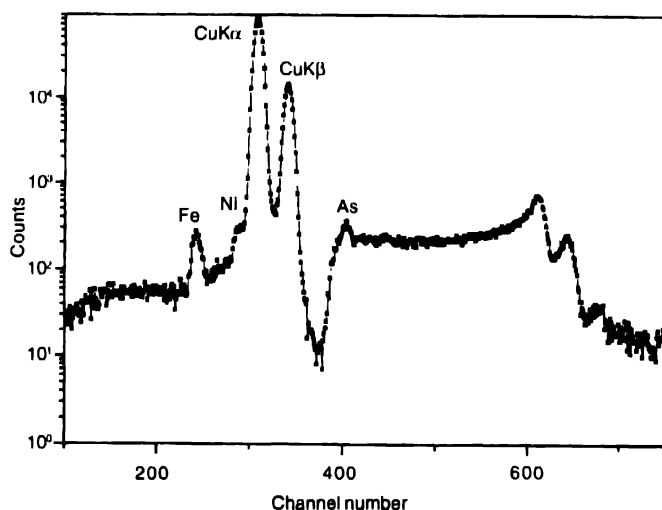
\* Corresponding Author

**Table 1.** PIXE results of coin samples (concentrations are in ppm)

Coin Code/ Elements	K	Ca	Ti	Cr	Fe	Co	Ni	Cu*	Zn	As
EIC-1	bdl	184.4	49.4	26.8	145.0	111.5	2210.6	93.205	bdl	2761.7
EIC-2	873.2	502.2	177.7	bdl	4191.7	134.6	856.0	94.209	bdl	545.0
BR-1	367.5	151.1	63.2	26.7	35.7	40.9	1248.4	95.124	14084.6	bdl
BR-2	1170.0	523	74.5	31.8	118.8	21.6	1620.8	95.325	5582.0	472.9
H-1	bdl	Bdl	45.5	bdl	172.1	119.8	1968.5	95.234	bdl	5542.9
G-1	118	393	31.0	37.9	42.9	70.3	1561.1	95.427	123.4	1723.7

\* = Percentage, bdl = below detection limit

are solely made up of copper with very low content of contaminants including K, Ca, Ti, Cr, Fe, Co, Ni, Zn, and As although some of these elements are missing in few cases. Two typical PIXE spectra are provided in Figures 1 and 2, which indicate the dominance of Cu K $\alpha$  and Cu K $\beta$  in the spectrum.

**Figure 1.** PIXE spectrum of a zinc-rich copper coin (BR-1)**Figure 2.** PIXE spectrum of an arsenic-rich copper coin (H-1)

From Table 1, it is evident that with increase time, for coins from EIC to British rule, the use of pure copper has increased significantly. However, the coins used during Holkar and Gwalior kings are of high purity (*i.e.*, 95.234 % and 95.427 %, respectively). The high content of arsenic in samples EIC-1, H-1 & G-1 strongly supports the use of sulfide ore for the preparation of these copper coins [2]. However, it should be mentioned here that in relation to copper artifacts, the elements like silver, bismuth, antimony and lead were the most important metallic impurities [11]. In this study, there was no detectable amount of these four elements, which is most significant as compared to other reports on various world copper coins [12-14]. But we should like to mention here that the present study indicating the absence of these four elements in copper coins is supported by the report of ancient work based on characterisation of ancient Indian Kushana coins [15]. Interestingly enough, a study using PIXE on Afghanistan copper material and ores [16] also support our findings. There in the ore of Malachite, containing 76.7% copper these four elements are absent. However, it is worth noting here that in case of arsenic-rich coins the presence of negligible amount of lead might have affected by the higher concentration of the former element due to the overlap of their K X-ray lines with their L X-ray lines. However, the present investigation will open the door for the characterization of ancient Indian coins to find out the chemical composition and various historical facts by using PIXE, which can effectively be used for interpreting various contemporary eco-sociological situations. Further work is in progress and will be reported in near future.

Preliminary PIXE investigation was carried out on some representative Indian copper coins. The elements K, Ca, Ti, Cr, Fe, Co, Ni, Zn, Cu and As were estimated by this technique. It was observed that the four elements namely silver, bismuth, antimony and lead are absent in these coins. The study indicates that PIXE can effectively be used for analysis of coins non-destructively.

#### Acknowledgments

PKN is thankful to IUC-DAEF, Calcutta center, Kolkata for providing him a research fellowship. Authors acknowledge

Mr T R Rautray, Ion Beam Laboratory for his help during the course of the present investigation.

## References

- M Hajivaliei, M L Garg, D K Handa, K L Govil, T Kakavand, V Vijayan, K P Singh, I M Govil *Nucl Instrum Meth.* **B150** 645 (1999)
- S A Junk, *Nucl. Instrum. Meth.* **B 181** 723 (2001)
- A Dacca, P Prati, A Zucchiatti, F Lucarelli, P A Mando, G Gemme, R Parodi and R Pera *Nucl Instrum Meth.* **B161-163** 743 (2000)
- P K Nayak, D Das, V Vijayan, P Singh and V Chakravorty *Nucl Instrum Meth.* **B 184** 649 (2001)
- V Vijayan, N Padhy and V S Ramamurthy *Indian J Phys* **70A** 237 (1996)
- P K Hota, V Vijayan and L P Singh *Indian J Phys* **75B** 333 (2001)
- W Maenhaut and K G Malmqvist *Hand Book of X-ray Spectrometry*, (Eds ) R Van-Grieken and A Markowicz, (New York Marcel Dekker) Chapter 11 p 517 (1992)
- [8] I Uzonyi, R Bugoi, A Sasianu, A Z Kiss, B Constantinescu and M Torbagyi *Nucl Instrum Meth.* **B161-163** 748 (2000)
- [9] J L Campbell, T L Hopman, J A Maxwell and Z Nezedky *Nucl Instrum Meth.* **B170** 193 (2000)
- [10] Z Smit, M Budnar, P Pelicon, B Zorko, T Knific, J Istemic, N Trampuz-Orel and G Demortier *Nucl Instrum Meth.* **B161-163** 753 (2000)
- [11] A M Friedman, M Conway, M Kastner, J Milsted, D Metta, P R Fields and E Olsen *Science* **152** 1504 (1966)
- [12] N Kallithrakas-Kanotos, A A Katsanos, A Aravantinos, M Oeconomides and I Touratsoglou *Archaeometry* **35** 165 (1993)
- [13] N Kallithrakas-Kanotos, A A Katsanos, C Potiradis, M Oeconomides and I Touratsoglou *Nucl Instrum Meth.* **B109/110** 662 (1996)
- [14] Y Haruyama, M Saito, T Muneda, M Mitai, R Yamamoto and K Yoshida *Int J PIXE* **9** 181 (1999)
- [15] M L Garg (2002) (private communication)
- [16] Th Berthoud, S Bonnefous, M Dechoux and J Francaix *British Occasional Paper No. 20* (ed ) P T Craddock, p87 (1980)